INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 33 (2008) 5020–5034

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Energy and material flow models of hydrogen production in the U.S. Chemical Industry

*Nesrin Ozalp**

Texas A&M University at Qatar, Mechanical Engineering Department, P.O. Box 23874 Education City, Doha, Qatar

ARTICLE INFO

Article history:
Received 2 March 2008
Received in revised form
29 May 2008
Accepted 29 May 2008
Available online 7 September 2008

Keywords:
Steam reforming
Hydrogen
Process
Energy allocation
Model

ABSTRACT

This paper gives energy and material flow models of hydrogen production via steam reforming of methane in the U.S. Chemical Industry. Two energy flow models are used to describe the allocation of energy among process end-uses. First, an energy end-use model is given, which was created based on actual operating data. Next, a representative material flow model is given on a national scale based on federal data on merchant hydrogen production. The last step is the energy process-step model, which was developed based on the steps described in the material flow model. Finally, the energy process-step model results are cross checked with the values found in the energy end-use model to justify that the selected representative hydrogen production material flow model does characterize the overall picture of hydrogen generation in the U.S. Chemical Industry. Results show the energy allocation among process steps in the form of steam, fuel and electricity. The major federal database to construct energy flow models is published once in four years. During the course of this study, the most recent U.S. federal energy database available was for the year 1998. Currently, the most recent available U.S. federal energy database is given for the year 2002.

1. Introduction

The major hydrogen production technique in industry is the steam reforming of natural gas [1–6]. The Economic Census, published every five years by the U.S. Census Bureau, gives the most comprehensive data on raw materials input and production output for manufacturing processes in the United States. If we refer to the latest available Current Industrial Report (CIR) [7], which is a production and shipments database published by the Census Bureau, we obtain the values shown in Table 1.

Table 1 shows that the total hydrogen production by the Industrial Gas Manufacturing subsector of the U.S. Chemical Industry in 2003 was increased by 22%, whereas a 35% increase is observed in the shipment. This shows that market demand for hydrogen as a commodity is significant. In order to identify the energy requirements for the production of that much hydrogen, energy inputs and outputs to each process step need to be found, which can be given by an energy process-step model.

Energy process-step model is a representation of energy flow for an industrial process. To construct it, first, the key energy consuming process steps need to be identified. Numerical values for each step of a process are obtained from thermodynamic principles and engineering analysis for a typical plant in the sector. In order to scale each process-step against national data, energy end-use model of that sector can be used since it gives allocation of energy to each end-use in

* Tel.: +974 4230250; fax: +974 4230011.
E-mail address: nesrin.ozalp@qatar.tamu.edu

0360-3199/$ – see front matter © 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2008.05.094

Table 1 – Commodity hydrogen production and shipment, kg

Chemical	2003		2004	
	Production	Shipment	Production	Shipment
Hydrogen	1.21×10^9	8.43×10^8	1.48×10^9	1.14×10^9

that sector on a national scale. The biggest challenge in modeling national scale energy process-step models for manufacturing industries is lack of consistent data sources that cover energy use by process step for each industrial sector.

There have been prior efforts to create energy process-step models [8–13]. For example, one of the initial and most comprehensive efforts to create material and energy flow models was developed at Drexel University for 108 different manufacturing processes, which are called Drexel models [8]. Drexel models were created based on data collected in 1976 and industrial process technology for that time period. The primary data collected to construct Drexel models were based on plant surveys and questionnaires, whereas industrial consultants, the Annual Survey of Manufacturers data published by the Census Bureau in 1976, and other reports were used as secondary data. Drexel Models have been used by government, industry and institutions since the 1980s. Due to the changes in technology, production practices, product composition, energy prices, and availability of data, Drexel models do not necessarily reflect current material and energy consumption patterns. However, some of these models still have the credibility in characterization of process steps or process flow for some of the manufacturing processes. For example, in one of their energy process-step models, Worrell et al. [9] utilize a Drexel model in order to give breakdown of energy consumption for an industrial process. They make an assumption for power generation efficiency to do the energy balance of a chemical manufacturing process, which brings an uncertainty to the analysis as they point out. Also, the electricity from cogeneration is not included into the industry total energy use presented in Ref. [9], which is a missing part in an energy analysis as some of the processes consume a large amount of electricity from cogeneration. Another example of energy flow model similar to this study was done by Wang et al. [10]. Their study was created based on Drexel model but for the Petroleum Refineries sector. In their analysis, they develop a refinery process flow chart based on data and process model taken from a Drexel model. In their results, they give ''energy based process energy allocation by final product'' per unit mass. Their results include mass, allocated energy use and energy intensity for each product manufactured in Petroleum Refineries sector. Wang et al. allocate energy use in terms of electricity, fuel and steam in the same way it is done in this study. Wang et al. include a market value-based process energy allocation by fuel for unit mass product manufactured, which provides an economic perspective. They also provide emissions from petroleum recovery, transportation, etc. Other studies that make use of Drexel models are those of Giraldo and Hyman and Andersen and Hyman [12,13]. The flow models in this study were constructed by further developing Refs. [12,13]. A thorough comparison and discussion about the differences between this study and Refs. [12,13] can be found elsewhere [14,15].

2. Hydrogen production

The U.S. Chemical Industry has 34 subsectors based on the industry classifications and descriptions defined by the North American Industrial Classification System (NAICS) [16]. There is a vast product composition manufactured by each of these subsectors, which constitutes the Chemical Industry as a whole. Within these 34 subsectors, hydrogen is mainly produced by the Industrial Gas Manufacturing subsector of the U.S. Chemical Industry. Acetylene, carbon dioxide, nitrogen, oxygen, argon, and fluorocarbons are also called ''industrial gases'' and are all produced by the Industrial Gas Manufacturing subsector. Although the majority of the industrial gases are produced by the Industrial Gas Manufacturing subsector, there are still other subsectors of the U.S. Chemical Industry producing industrial gases as given in Table 2 [17]. Since hydrogen is an industrial gas, this table basically shows us all subsectors producing hydrogen along with other industrial gases. Therefore, 92% of the hydrogen is produced by the Industrial Gas Manufacturing (NAICS 325120) subsector.

The major hydrogen production technique in industry is the steam reforming of natural gas [1–6], which is the most practical and economical known process to meet the world market demand for hydrogen. Therefore, the energy process-step model for hydrogen production will be constructed based on steam reforming of the methane process. Since the energy end-use model is the key to establish energy process-step model, we need to create an energy end-use model for the Industrial Gas Manufacturing sector first. The following sections are devoted to establishing an energy end-use of NAICS 325120.

3. Energy end-use model

Constructing an energy end-use model includes creating two tables: energy utilization and end-use. The energy utilization table gives the type of fuels used, whereas the end-use table provides allocation of these fuels to end-uses. The primary federal data to construct these tables is the Manufacturing

Table 2 – Industries producing industrial gases, 1997, M$ [16]

Industry	Value	% in Total
Industrial gas manufacturing	4791	92
Plastics material and resin manufacturing	162	3
Other basic organic chemical manufacturing	135	3
Petrochemicals	89	2
Nitrogenous fertilizer manufacturing	26	<1
Total	5203	100

Table 3 – Inputs for heat, power and electricity generation in Industrial Gas Manufacturing sector in 1998, PJ

MECS source	Energy form	Industrial Gas Manufacturing NAICS 325120
Table N3.2.	*Total*	193 ± 8
	Net electricity	117 ± 5
	Residual fuel oil	0
	Distillate fuel oil	*
	Natural gas	66 ± 4
	LPG and NGL	*
	Coal	0
	Coke and breeze	0
	Other	9
Table N5.1.	*Total byproducts*	1
	Blast furnace/ coke oven gases	0
	Waste gas	1
	Petroleum coke	0
	Pulping liquor or black liquor	0
	Wood chips, bark	0
	Waste oils, tars and waste materials	0
Table N13.1.	*Net demand for electricity*	119 ± 3
	Purchases	113 ± 7
	Transfers in	Q
	Total onsite generation	2
	Sales and/or transfers offsite	0
Table N13.2.	*Total onsite generation*	2
	Cogeneration	2
	Renewable energy (excluding wood and other biomass)	0
	Other	Q
Table N11.3.	*Steam purchased*	6 ± 0.2

Energy Consumption Survey (MECS) by the Energy Information Administration of the U.S. Department of Energy [18]. The main reason for choosing this database as a primary data source is because it provides data for each industry very comprehensively and the industry classification codes used in this database are being used by other federal databases on materials and emissions as well. This provides a consistency in creating energy, material and emission models for the industry of interest on a national scale. An additional constructive aspect of using this database is: ''this data is derived from a single source, the double counting issue is minimized and the boundary line between industries is clear.'' [10]. Other databases, such as those maintained by trade associations or other private databases, may not put facilities that are classified as Industrial Gas Manufacturing by MECS under the same category. As a result, MECS energy inputs and/or outputs for one particular industry may differ compared to other databases because of the differences in classification of plants and industries. A thorough discussion and information on the advantages and the gaps of the MECS database can be found in Ref. [19].

During the course of this study, the most recent MECS data available were for the year 1998. Currently, the most recent MECS data are given for the year 2002 based on the data collected from 15,500 establishments. Collection of the 2006 data has been completed and it is in the process of statistical analysis and sorting.

3.1. *Energy utilization table*

Data to construct energy utilization table is obtained from the following five different MECS tables:

MECS *Table N5.1:* Selected byproducts in fuel consumption
MECS *Table N3.2:* Fuel consumption
MECS *Table N11.3:* Quantity of purchased electricity, natural gas, and steam
MECS *Table N13.1:* Electricity: components of net demand
MECS *Table N13.2:* Electricity components of onsite generation

Some of the data in these tables are withheld by MECS to avoid disclosing data of individual establishments, and they are denoted by W. Also, the numerical values <0.5 PJ are indicated by *. Contributions of these values are included in higher level totals. In addition, some of the values in these MECS tables are denoted by Q. This represents the data withheld because the relative standard error is greater than 50%. The energy utilization table of the U.S. Industrial Gas Manufacturing sector was constructed using the MECS tables listed earlier, and it is given in Table 3. The values presented in this table include the sampling uncertainties of the MECS data with 95% confidence interval and the numbers centered in the table are column totals within each MECS table. As it is seen in Table 3, the values that have the highest uncertainty are ''electricity purchase'', and ''natural gas'' consumption with a 6% uncertainty. On the other hand, the ''total energy consumption'' and the ''net electricity consumption'' values have about 4% uncertainty, whereas ''net demand for electricity'' has about 3%. The rest of the values have either zero or very small uncertainties.

3.2. *Energy end-use data*

The construction of the energy end-use table requires the utilization of these MECS tables:

MECS *Table N6.2:* End uses of fuel consumption
MECS *Table N6.4:* End uses of fuel consumption

Although these MECS tables have the same title, there are two differences between them. First, Table N6.2 includes ''net electricity'' whereas Table N6.4 gives ''net demand for electricity''. ''Net demand for electricity'' is the total amount of electricity used. ''Net electricity'' is the sum of the purchases, transfers in, and generation of electricity from noncombustible renewable sources, minus electricity sold and transferred out. It does not include onsite electricity generation from combustible fuels because that energy has already been included as fuel input such as coal.

$$\text{Net electricity} = \text{Electricity (purchases} - \text{sales)} + \text{Electricity from noncombustible renewables} \quad (1)$$

Second, Table N6.2 has an additional column for "Other" which includes net steam (the sum of purchases, generation from renewables, and net transfers) and other energy that respondents of the MECS survey indicated was used to produce heat and power.

$$\text{Other} = \text{Byproducts} + \text{Steam (purchases} - \text{sales)} + \text{Steam from noncombustible renewables} + \text{Fuels not listed separately} \quad (2)$$

where the "Byproducts" component is disaggregated in MECS Table N5.1. Also, MECS Table N13.1 shows the components of the "Net demand for electricity." If we use the terms "purchases" and "sales" to include electricity transfer transactions, then we can write that

$$\text{Net demand for electricity} = \text{Electricity (purchases} - \text{sales)} + \text{Total onsite generation} \quad (3)$$

The net steam is defined analogous to the "net electricity" definition in Eq. (1), i.e.

$$\text{Net Steam} = \text{Steam (purchases} - \text{sales)} + \text{Steam from noncombustible renewables} \quad (4)$$

The "transfers in" are also included in purchases. Then, substitution of Eq. (4) into Eq. (2) results in

$$\text{Other} = \text{Byproducts} + \text{Net Steam} + \text{Fuels not listed separately} \quad (5)$$

If we account for boiler efficiency when producing steam onsite from combustible energy forms with an assumption that "net steam" goes directly to end-uses, the above equation can be rewritten as

$$\text{Other} = \text{Other energy sources except net steam} + \text{Net steam} \quad (6)$$

where

$$\text{Other energy sources except net steam} = \text{Byproducts} + \text{Fuels not listed separately} \quad (7)$$

It should be noted that the MECS definition of the conventional electricity generation item in these MECS tables is: electricity generation via gas turbines or piston engines, not via steam turbines.

3.3. *Energy end-use table extracted from the database*

End-use data table for the U.S. Industrial Gas Manufacturing sector was constructed using the MECS tables listed earlier, and it is given in Table 4. The values presented in this table include the uncertainty of the MECS data and the numbers centered in the table are column totals within each MECS table. In Table 4, the value that has the highest uncertainty is "Total net electricity consumption" with about 13% uncertainty. The second highest uncertainty is "Net electricity" consumption for machine drive, which is about 10%. The rest of the values in Table 4 have uncertainties which are less than 10%.

3.4. *Filling in the missing values in Tables 2 and 3*

Before constructing the energy end-use models, the missing parts in Tables 2 and 3 must be filled in. The key steps and assumptions in dealing with missing MECS data in these tables are given below.

Table 4 – End-use data for NAICS 325120 in 1998, extracted from MECS Tables N6.2 and N6.4, PJ

	Total	Net electricity	Residual fuel oil	Distillate oil and diesel fuel	Natural gas	LPG	Coal (excluding coal coke and breeze)	Other	Net demand for electricity
Total fuel consumption	193 ± NA	117 ± 15	0	*	66 ± 5	*	0	9 ± NA	19 ± 14
Indirect uses (boiler fuel)	–	*	0	*	27 ± 3	*	0	–	*
Direct uses (total process uses)	–	114 ± 10	0	*	37 ± 2	*	0	–	16 ± 10
Process heating	–	1 ± 0.1	0	0	22 ± 1	*	0	–	1 ± 0.1
Process cooling and refrigerating	–	3 ± 0.3	0	0	0	0	0	–	3 ± 0.3
Machine drive	–	108 ± 13	0	*	15 ± 1	*	0	–	110 ± 13
Electrochemical processing	–	1 ± 0.04	–	–	–	–	–	–	1 ± 0.04
Other process uses	–	*	0	0	*	0	0	–	*
Direct Uses (Total non-process use)	–	3 ± 0.3	0	*	2 ± 0.1	*	0	–	4 ± 0.4
Facility HVAC	–	2 ± 0.5	0	*	*	*	0	–	2 ± 0.4
Facility lighting	–	1 ± 0.03	–	–	–	–	–	–	2 ± 0.1
Facility support	–	*	0	0	2 ± 0.03	*	0	–	*
Onsite transportation	–	0	–	*	0	*	–	–	0
Conventional electricity generation	–	–	0	*	*	0	0	–	–
Other non-process use	–	*	0	0	0	0	0	–	*
End-use (NR)	9 ± NA	*	0	0	0	0	0	9 ± NA	*

NA, not available; NR, not reported.

The withheld data in Table 3 for ‘‘Transfers in’’, and ‘‘Other onsite generation’’ are denoted by Q. These can be calculated by checking the column balance. The other missing values in Table 3 are *, which are converted to zero. This completes filling in the missing values in Table 3.

The next step is to fix the missing values in Table 4. First, the ‘‘Net Electricity’’ and ‘‘Net Demand for Electricity’’ columns for ‘‘Process uses’’ do not balance. The missing 1 PJ of electricity consumption in both columns can be attributed to ‘‘Machine Drive’’ as it is the biggest electricity consumer among the direct process uses category. This 1 PJ correction creates less that 1% difference in the actual reported ‘‘Machine Drive’’ electricity consumption. There is 9 PJ ‘‘Not reported end-use’’ values for ‘‘Other’’ fuels. This can be distributed among the boiler and the end-use by using the total fuel distribution ratio. The conversion of the missing values in Table 4 is completed by converting all asterisks to zero.

Allocation of net steam among end-uses was made based on the total fuel ratio among the end-uses, e.g.

Total fuel consumption for process uses = 37 PJ

(1) Process heating accounts for 59% of this total;
(2) Process cooling and refrigerating accounts for 0% of this total;
(3) Machine Drive accounts for 41% of this total;
(4) Electro-chemical processes account for 0% of this total;
(5) Other process uses account for 0% of this total.

Total fuel consumption for non-process uses = 2 PJ

(1) HVAC accounts for 0% of this total;
(2) Facility lighting accounts for 0% of this total;
(3) Facility support accounts for 100% of this total;
(4) Onsite transport accounts for 0% of this total;
(5) Conventional electricity generation accounts for 0% of this total;
(6) Other non-process uses account for 0% of this total.

The process and non-process uses consume 39 PJ fuel, 95% of which goes to process uses, whereas 5% goes to non-process uses. The adjusted MECS end-use data for the Industrial Gas Manufacturing sector is given in Table 5.

3.5. *Allocation of steam and waste heat to end-uses*

Tables 2 and 4 do not provide any information about the steam and recovered waste heat allocation among the end-uses. Therefore, an assumption must be made on the allocation of steam and recovered waste heat among the end-uses in the Industrial Gas Manufacturing sector. In this study, it was assumed that the allocation of the fuels to end-uses is the same as the allocation of steam and recovered waste heat among the end-uses. These ratios are given earlier in Section 3.4. In order to get data on the net useful thermal energy distribution among the end-uses, Energy Information Administration (EIA) 860B database was referred [20]. However, EAI 860B does not provide that data except for few facilities. If we still refer to those few facilities to have an idea about the actual distribution of recovered waste heat, we see that the process heating is the dominant application. This supports the assumption made in

Table 5 – Adjusted end-use data for NAICS 325120 in 1998, PJ

	Total	Net electricity	Residual fuel oil	Distillate oil and diesel fuel	Natural gas	LPG	Coal (excluding coal coke and breeze)	Other	Net demand for electricity
Total fuel consumption	193 ± NA	117 ± 15	0	0	66 ± 5	0	0	9 ± NA*	120 ± 14
Indirect uses (boiler fuel)	–	0	0	0	27 ± 3	0	0	1 ± NA	0
Direct uses (total process uses)	–	114 ± 10	0	0	37 ± 2	0	0	0	116 ± 10
Process heating	–	1 ± 0.1	0	0	22 ± 1	0	0	0	1 ± 0.1
Process cooling and refrigerating	–	3 ± 0.3	0	0	0	0	0	0	3 ± 0.3
Machine drive	–	109 ± 13	0	0	15 ± 1	0	0	0	111 ± 13
Electrochemical processing	–	1 ± 0.04	0	0	0	0	0	0	1 ± 0.04
Other process uses	–	0	0	0	0	0	0	0	0
Direct uses (Total non-process use)	–	3 ± 0.3	0	0	2 ± 0.1	0	0	0	4 ± 0.4
Facility HVAC	–	2 ± 0.5	0	0	0	0	0	0	2 ± 0.4
Facility lighting	–	1 ± 0.03	0	0	0	0	0	0	2 ± 0.1
Facility support	–	0	0	0	2 ± 0.03	0	0	0	0
Onsite transportation	–	0	0	0	0	0	0	0	0
Conventional electricity generation	–	0	0	0	0	0	0	0	0
Other non-process use	–	0	0	0	0	0	0	0	0
End-use (NR)	0	0	0	0	0	0	0	8	0

NA, not available; NR, not reported.
*9 PJ = 1 PJ (to the boiler and conventional electricity generation) + 8 PJ (net steam to end-uses) from Eq. (5). Since the net steam in the end-use model distributed separately from the fuel inputs, allocation of the net steam among the end-uses is not shown in the table.

Giraldo and Hyman [12]. Fig. 1 gives the steam and waste heat allocation among end-uses in the Industrial Gas Manufacturing sector in 1998 along with the fuel and electricity allocation among the end-uses. Fig. 1 is the key to construct energy process-step model as it shows fuel, steam, waste heat and electricity inputs to each process.

3.6. Building the end-use model

The following sections describe the details of constructing the end-use model given in Fig. 2.

3.6.1. Fuel inputs in the model

The input values of residual fuel oil, distillate fuel oil, natural gas, LPG and NGL, coal, and coke and breeze from Tables 2 and 4 are located in the lower left corner of Fig. 2. From Eq. (5), we know that "Other" fuels include net steam. Since the "Net steam" is modeled separately, "Other energy sources except net steam" is located in the lower left corner of Fig. 2.

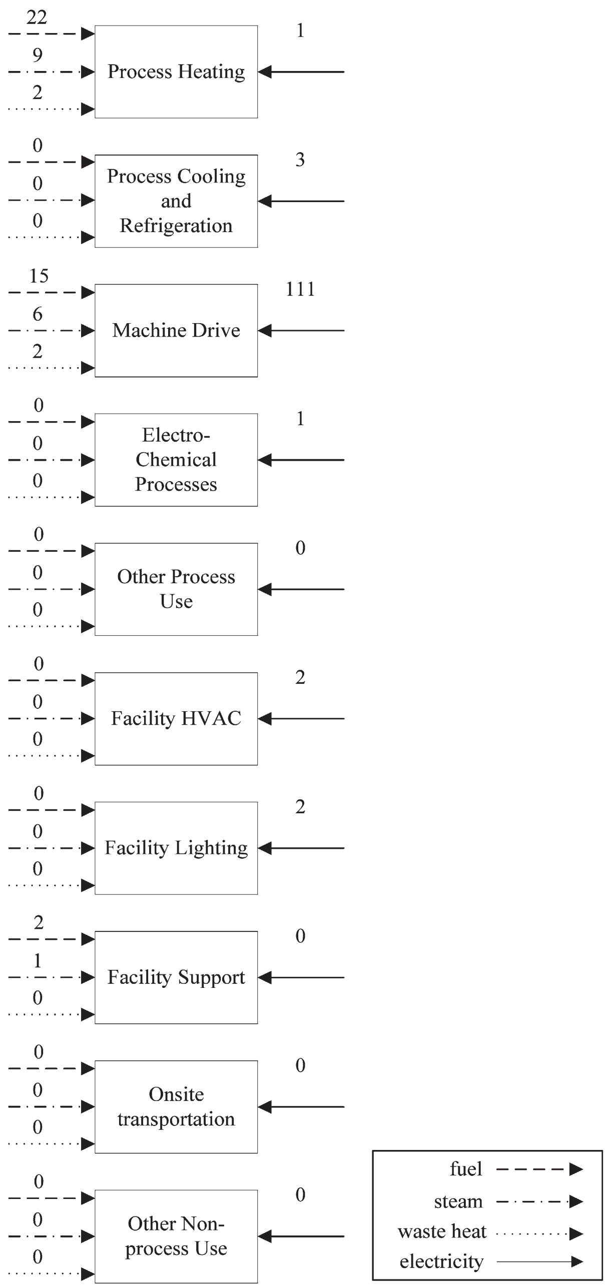

Fig. 1 – Fuel, steam, waste heat and electricity allocation among end-uses in industrial gas manufacturing, 1998, PJ.

3.6.2. Allocation of fuels and electricity to end-uses

Tables 2 and 4 provide allocations of fuels and electricity to end-uses. Electricity allocation among the end-uses is located on the right side of the process and non-process uses column, whereas fuel allocation among the end-uses are located on the left side.

3.6.3. Allocation of net steam to end-uses

By using the Eq. (5) and assuming that the "Fuels not listed separately" is zero, the net steam for industrial gas manufacturing is found as:

$$\text{NetSteam} = 8\,\text{PJ} \tag{8}$$

The net steam is located in the left column of Fig. 2. The allocation of the net steam to end-uses is made based on the fuel distribution ratios given earlier in Section 3.4.

3.6.4. Offsite electricity

The acquisition and disposition of electricity is presented in the upper left corner of Fig. 2 as purchased electricity, electricity sold and electricity from noncombustible renewables. These values are taken from Table 3 and they do not include onsite power generation from combustible fuels.

3.6.5. Steam loss

Steam distribution losses due to heat transfer, ineffective steam traps, leaks, etc. vary from 20% to 40% [21–23]. In this energy end-use model, it was assumed that the steam loss during distribution is 30%.

3.7. Energy end-use model of the industrial gas manufacturing

Since there is insufficient information to build onsite steam and power generation for the Industrial Gas Manufacturing sector, the intermediate energy conversion efficiencies that are found for the U.S. Chemical Industry in our earlier studies were assumed to be the same for the Industrial Gas Manufacturing sector. The intermediate onsite steam and power conversion efficiencies for the U.S. Chemical Industry can be found in Ozalp and Hyman [24]. Therefore, the efficiencies given in Ref. [24] were applied to calculate the recovered waste heat and steam production in this sector. The calculations with the revision to the onsite steam and power model in Ref. [24] and data extracted from MECS yields Fig. 2. It should be noted that there is 1 PJ unbalance for the electricity input due to the rounding off adjustment made on the machine drive electricity input as discussed earlier in Section 3.4. The "transfer ins" are also included in purchases. Therefore, the total purchased electricity is the summation of 113 PJ purchased electricity and 4 PJ transfers in from Table 3, which gives 117 PJ.

As can be seen from the energy end-use model in Fig. 2, fuel input is distributed among onsite power and steam generation and end-uses. About 42% of the fuel input goes to onsite steam and power generation whereas, 58% directly goes to end-uses.

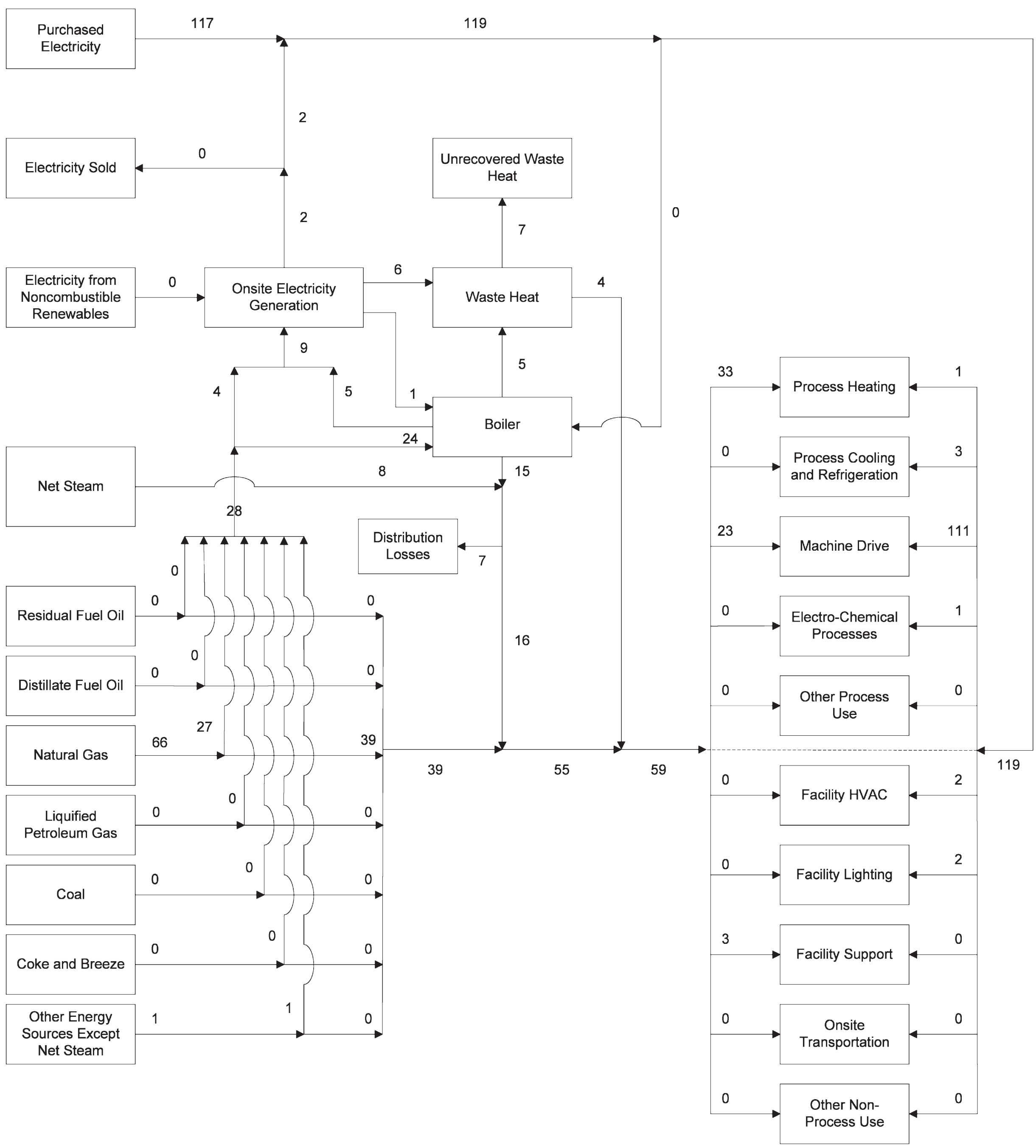

Fig. 2 – Energy end-use model of the industrial gas manufacturing in 1998, PJ.

All of the fuel to onsite steam and power goes to the boiler. Therefore, this subsector does not use fuel directly for power generation. Instead, power is generated onsite by the steam input from the boiler.

The Industrial Gas Manufacturing sector meets less than 2% of its electricity needs via onsite power generation. Accounting for 98% of the total electricity to end-uses, purchased electricity is the key contributor. It is also seen in Fig. 2 that 45% of the boiler input directly goes to end-uses, whereas 20% goes to waste heat and the rest to onsite electricity generation. We can also see that contribution of the boiler to the end-uses is bigger than that of net steam.

Although 23 PJ of energy goes to end-uses from boiler and net steam combined, 30% of this amount is lost due to distribution. Overall, 72% of the fuel and net steam input goes to end-uses. We can see that 59 PJ is supplied to end-uses by total fuel, steam and waste heat input. On the other hand, there is 119 PJ supplied to end-uses by onsite electricity and purchased electricity combined. This shows that fuel input for onsite power and steam generation combined with net steam does not make a big contribution to the end-uses through steam production and waste heat recovery.

Since we now know the allocation of energy among the "process end-uses" in the Industrial Gas Manufacturing sector, we can use that information to create an energy process-step model for any chemicals produced by this industry. In this study, we are interested in hydrogen production. Therefore, we want to allocate the energy values in Figs. 1 and 2 among the process steps of hydrogen production process. To be able to allocate steam, fuel, electricity and waste heat among the process steps of hydrogen production, we need to identify the steps of hydrogen production process. Earlier, we stated that the "steam reforming of methane" is the representative hydrogen production process. Therefore, we can take the steps of that process and allocate the energy values in Figs. 1 and 2 among each process step accordingly. However, process steps of steam reforming of methane may change from one manufacturing plant to another. Hence, a "representative" process flow for steam reforming of methane process should be taken as reference. In this study, hydrogen production process flow given in the Drexel models is taken as the "representative hydrogen production process". The following section is devoted for the development of national scale hydrogen production process flow model based on the data and the process flow given in the Drexel model.

4. Process steps and material flow model of hydrogen production

The representative commercial hydrogen manufacturing technique in this study is taken from the Drexel model [7]. A simplified form of this process is given by Simpson and Lutz [25] along with exergy analysis of each component for the detailed process flow. Material flow model of hydrogen production in Fig. 3 shows each step of steam reforming of methane on a national scale. The process flow in Fig. 3 is created based on a mass balance around each process step. This figure provides an overall national picture of material inputs and outputs for hydrogen production in 1998. The data on material inputs and outputs for each of the representative production processes given in Fig. 3 is obtained from the Current Industrial Report (CIR) of the U.S. Census Bureau [26]. It should be noted that the "hydrogen production" values in this database "excludes amounts vented, used as fuel, etc., and amounts produced and consumed in the manufacturing of synthetic ammonia and methanol, but includes amounts produced for sale or interplant transfer to plants consuming this gas in the production of ammonia. Also excludes amount produced by ammonia dissociation process (cracking of ammonia). Also excludes amounts produced in petroleum refineries for captive use." [26]. Comparison of the inputs and outputs of the reference of this model with another hydrogen production material flow model is given in Table 6 for unit mass hydrogen production.

Water consumption reported in Ref. [6] is 24% for reforming and shift reactions, 71.22% for steam production, and 4.8% for other process steps. As for the water emissions, it is stated that a quantitative value is not reported since the amount was very small.

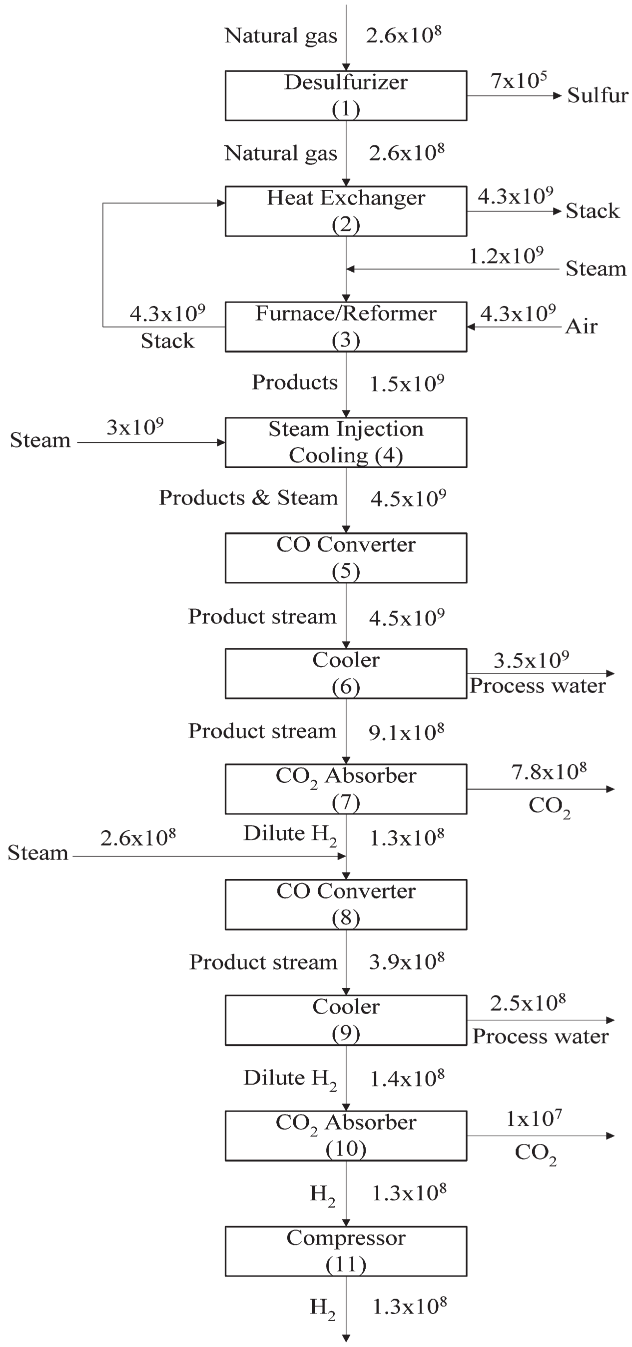

Fig. 3 – Representative process flow of hydrogen production in 1998, kg.

5. Energy process-step model

An energy process-step model of a product on a national scale is generated following this methodology:

(1) Search and selection of a representative manufacturing process;
(2) Description of the representative manufacturing process;

Table 6 – Comparison of the inputs, products and emissions per kg hydrogen produced, kg

	Reference of this model [7]	Koroneos et al. [6]
Process	Steam reforming of natural gas	Steam reforming of natural gas
Purity	–	99.95%
Inputs		
Natural gas	2	2.09
Air	33	NA
Steam	9	6.91
Product		
Hydrogen	1	1
Emissions		
H_2O	29	–
CO_2	6	10.66
Benzene	–	0.0014
CO	–	0.0059
CH_4	–	0.146
NO_x	–	0.0126
N_2O	–	4×10^{-5}
Non-methane hydrocarbons	–	0.0263
Particulates	–	0.002
SO_x	–	0.0097

NA, not available in the report.

(3) Identification of energy inputs in the representative manufacturing process per unit mass of output;
(4) Scaling of the energy inputs in the unit mass representative manufacturing process based on national level production;
(5) Reconciliation of national scale manufacturing process with the end-use model based on federal data.

The first two steps for industrial gases were provided in previous sections of this paper. Therefore, this section focuses on steps 3–5.

The representative hydrogen production process via steam reforming of methane is given in Fig. 3 on a national scale for the year 1998. There are 11 process steps to allocate steam, fuel, electricity and waste heat that we found in Figs. 1 and 2. The MECS-based end-use model in Fig. 1 for industrial gases provides a suitable foundation to scale the values given in Fig. 3. However, the end-use model is not given for each product, but as a summation of energy consumption for manufacturing all products in the Industrial Gas Manufacturing sector. Therefore, the values in the end-use model must be broken down for each product so that we can find how much of that total energy goes to hydrogen production. Eq. (9) gives us the summation of the energy consumption for each industrial gas.

$$\sum(\text{End-uses}_{CO_2} + \text{End-uses}_{N_2} + \text{End-uses}_{O_2} + \text{End-uses}_{C_2H_2} + \text{End-uses}_{Ar} + \text{End-uses}_{H_2} + \text{End-uses}_{\text{Fluorocarbons}}) = \text{End-use values} \quad (9)$$

Additionally, the end-use values must be further broken down among process steps. Briefly, in order to be able to scale the values in Figs. 1 and 2, the end-use values must be divided two dimensionally: among products and among process steps. In order to divide the energy allocation values in Figs. 1 and 2, we need to use the ‘‘process end-use’’ part of Figs. 1 and 2, because we are looking for energy allocation for process use, not for ‘‘non-process’’ use. Fig. 4 gives the fuel, steam, waste heat and electricity allocation among the process end-uses. This figure was basically extracted from the process end-uses part of Fig. 1. In order to divide these values among each products of the Industrial Gas Manufacturing sector, the breakdown procedure explained in the following section should be done.

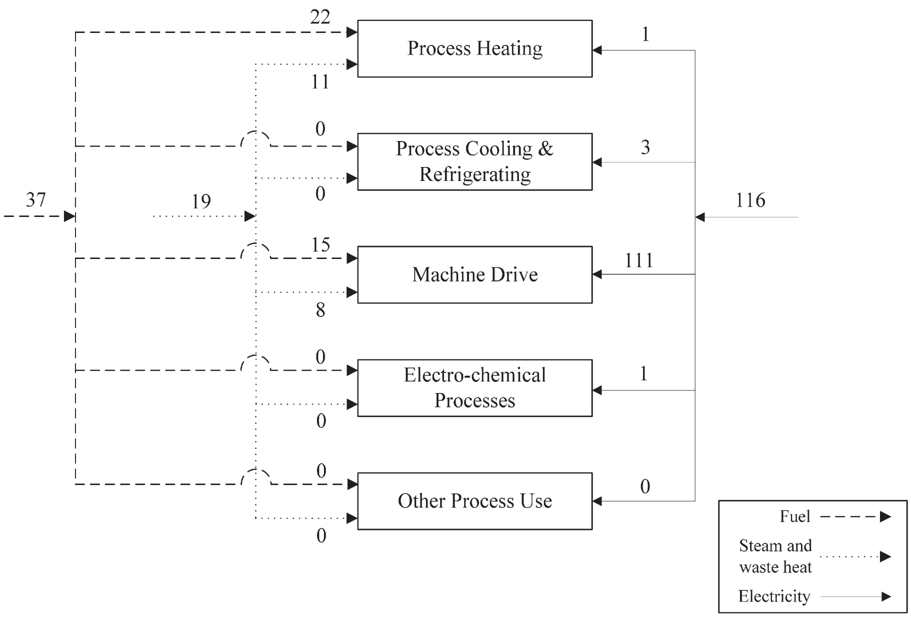

Fig. 4 – Allocation of fuel, steam, waste heat and electricity among process end-uses in 1998, PJ.

5.1. *Breakdown procedure of the fuel, steam, waste heat and electricity values*

The fuel (F) consumption values assigned to process heating (PH) can be represented as follows:

$$\text{Fuel consumption for Process Heating}_{\text{Hydrogen}} = Q_{PH-F} \tag{10}$$

$$\text{Fuel consumption for Process Heating}_{CO_2} = X_{PH-F} \tag{11}$$

$$\text{Fuel consumption for Process Heating}_{O_2} = Y_{PH-F} \tag{12}$$

$$\text{Fuel consumption for Process Heating}_{N_2} = Z_{PH-F} \tag{13}$$

$$\text{Fuel consumption for Process Heating}_{\text{Argon}} = P_{PH-F} \tag{14}$$

$$\text{Fuel consumption for Process Heating}_{\text{Acetylene}} = W_{PH-F} \tag{15}$$

$$\text{Fuel consumption for Process Heating}_{\text{Fluorocarbon}} = R_{PH-F} \tag{16}$$

The summation of them gives the ''total fuel (F) consumption for process heating (PH)'', which can be written as follows:

$$Q_{PH-F} + X_{PH-F} + Y_{PH-F} + Z_{PH-F} + P_{PH-F} + W_{PH-F} + R_{PH-F} = F_{PH} \tag{17}$$

We can demonstrate the electricity (E) consumption values assigned to process heating using a similar notation described above. Then this results with ''total electricity consumption for process heating'':

$$Q_{PH-E} + X_{PH-E} + Y_{PH-E} + Z_{PH-E} + P_{PH-E} + W_{PH-E} + R_{PH-E} = E_{PH} \tag{18}$$

Similarly, the ''total steam & waste heat (S&WH) consumption for process heating'' can be represented as follows:

$$Q_{PH-SWH} + X_{PH-SWH} + Y_{PH-SWH} + Z_{PH-SWH} + P_{PH-SWH} + W_{PH-SWH} + R_{PH-SWH} = SWH_{PH} \tag{19}$$

Eqs. (10)–(19) give us the total amount of fuel, steam & waste heat and electricity consumption for ''*Process Heating*'' during the manufacturing process of each industrial gas. We can write down the total amount of fuel, steam & waste heat and electricity consumption for other process end-uses in Fig. 4 – namely ''*Process Cooling & Refrigerating*'', ''*Machine Drive*'', ''*Electro chemical Processes*'' and ''*Other Process Use*'' – in the same way.

Therefore, ''the total fuel (F) consumption for process cooling and refrigerating (PC&R)'' is given as:

$$Q_{PCR-F}+X_{PCR-F}+Y_{PCR-F}+Z_{PCR-F}+P_{PCR-F}+W_{PCR-F}+R_{PCR-F}=F_{PCR} \tag{20}$$

Similarly, ''the total electricity (E) consumption for process cooling and refrigerating'' is given as:

$$Q_{PCR-E}+X_{PCR-E}+Y_{PCR-E}+Z_{PCR-E}+P_{PCR-E}+W_{PCR-E}+R_{PCR-E}=E_{PCR} \tag{21}$$

We can demonstrate ''the total steam & waste heat (S&WH) consumption for process cooling and refrigerating'' as follows:

$$Q_{PCR-SWH}+X_{PCR-SWH}+Y_{PCR-SWH}+Z_{PCR-SWH}+P_{PCR-SWH}+W_{PCR-SWH}+R_{PCR-SWH}=SWH_{PCR} \tag{22}$$

We can write the ''total fuel (F) consumption'', ''total steam & waste heat (S&WH) consumption'' and ''total electricity (E) consumption'' for ''Machine Drive (MD)'', ''Electro Chemical Processes (ECP)'' and ''Other Process Uses (OPU)'' in the same way. In order to meet the maximum allowable page limit, those equations are not given in this paper. But one can refer to Ozalp [27] for those equations and all details of the breakdown procedure for other industrial gases.

Now, we can refer to Fig. 4 to write the corresponding values for the following:

→ F_{PH} (total fuel for process heat)
→ E_{PH} (total electricity for process heat)
→ $S\&WH_{PH}$ (total steam & waste heat for process heat)
→ $F_{PC\&R}$ (total fuel for process cooling & refrigeration)
→ $E_{PC\&R}$ (total electricity for process cooling & refrigeration)
→ $S\&WH_{PC\&R}$ (total steam and waste heat for process cooling & refrigeration)
→ F_{MD} (total fuel for machine drive)
→ E_{MD} (total electricity for machine drive)
→ $S\&WH_{MD}$ (total steam & waste heat for machine drive)
→ F_{ECP} (total fuel for electro-chemical process)
→ E_{ECP} (total electricity for electro-chemical process)
→ $S\&WH_{ECP}$ (total steam & waste heat for electro-chemical process)
→ F_{OPU} (total fuel for other process uses)
→ E_{OPU} (total electricity for other process uses)
→ $S\&WH_{OPU}$ (total steam & waste heat for other process uses)

Therefore, the energy end-use model gives us the following values for the total fuel consumption by each process:

$$F_{PH} = 22\ \text{PJ} \tag{23}$$

$$F_{PH} = 22\ \text{PJ} \tag{24}$$

$$F_{PCR} = 0\ \text{PJ} \tag{25}$$

$$F_{MD} = 15\ \text{PJ} \tag{26}$$

$$F_{ECP} = 0\ \text{PJ} \tag{27}$$

$$F_{OPU} = 0\ \text{PJ} \tag{28}$$

As for the total steam and waste heat consumption by each process, Fig. 4 gives us the following:

$$F_{PH} = 11\ \text{PJ} \tag{29}$$

$$F_{PCR} = 0\ \text{PJ} \tag{30}$$

$$F_{MD} = 8\ \text{PJ} \tag{31}$$

$$F_{ECP} = 0\ \text{PJ} \tag{32}$$

$$F_{OPU} = 0\ \text{PJ} \tag{33}$$

Finally, the total electricity consumption by each process is given as follows by referring to Fig. 4:

$$F_{PH} = 1\ \mathrm{PJ} \tag{34}$$

$$F_{PCR} = 3\ \mathrm{PJ} \tag{35}$$

$$F_{MD} = 111\ \mathrm{PJ} \tag{36}$$

$$F_{ECP} = 1\ \mathrm{PJ} \tag{37}$$

$$F_{OPU} = 1\ \mathrm{PJ} \tag{38}$$

Now we know how much fuel, for example, was consumed for process heat, which is given in Eq. (23) as well as it can be seen in Fig. 4. However, this total is the fuel amount consumed for the production of all industrial gases. Therefore, we need additional information that tells us how much of that 22 PJ goes to hydrogen production. We can get that information from Drexel models.

We already took the hydrogen material process-step model from the Drexel and scaled it against the national data to have hydrogen production material flow model for the year 1998. We can refer to the same Drexel model for energy consumption values by each process step.

The energy values in the Drexel are given in terms of intensity (energy per mass). Since we know the total hydrogen production from the CIR data, we can scale the energy intensity values accordingly so that we obtain energy consumption by each process step, which is given in Fig. 5. Therefore, we referred to Drexel models again for the allocation of energy among each process step. However, although Fig. 5 gives us the consumption of fuel, steam, waste heat and electricity by each process step of hydrogen production, we need to double check these values with another source. That source would be the energy end-use model in Fig. 4. As we know, Fig. 4 gives us the "total" energy consumption. Therefore, it does not tell us the energy consumption specifically by hydrogen production.

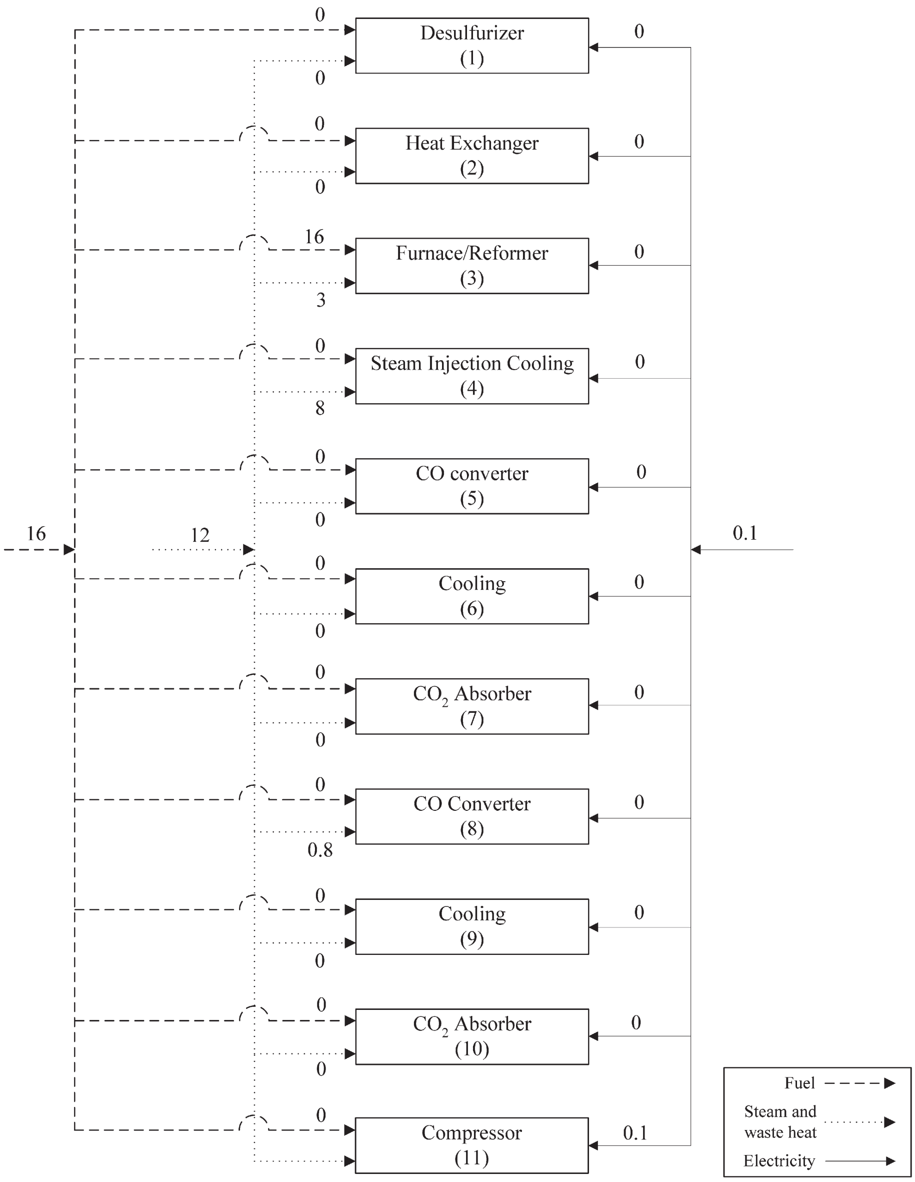

Fig. 5 – Energy process-step model of hydrogen production in 1998, PJ.

In order to know the share of consumption for hydrogen production in that total, we need to create energy process-step models for all of the industrial gases, so that we can compare the numbers we get from those process-step models vs. energy end-use model. That would also tell us if the numbers in Fig. 5 are reasonable. Therefore, the next step is to verify the model given in Fig. 5 by cross checking the energy end-use model values with the energy process-step models values.

6. Validation of the energy process-step model of hydrogen production given in Fig. 5

Energy process-step model of hydrogen production in Fig. 5 was developed from the Drexel model for hydrogen production. In order to verify if these numbers are reasonable, they should be compared with another data source. Energy end-use model given in Figs. 1 and 2 were developed using the MECS database. Therefore, the source of the energy end-use model is the MECS, which reflects actual operating data values. On the other hand, Fig. 5 gives the numbers based on a scaling made by combining Drexel model and CIR database. However, the numbers in Fig. 5 are given only for the hydrogen production, whereas the energy end-use model values are given for the summation of all industrial gases. Therefore, in order to be able to compare the numbers in Fig. 5, we need similar energy process-step models for all industrial gases.

Since the focus of this paper is the ''hydrogen'', energy process-step models for other industrial gases are not given in here but they can be found in Ref. [27]. The summary of the energy process-step models for all industrial gases is taken from Ref. [27] and given in Table 7. Table 7 enables us to compare the energy consumption estimates in Fig. 2 with the energy consumption estimates given in Fig. 5 and the energy consumption estimates given in Ozalp [27] for the other industrial gases.

As it is seen, there are many missing pieces in Table 7. However, it still gives us an insight about the energy consumption during industrial gas manufacturing and how close the estimates in energy process-step models of industrial gases compared to the estimates in energy end-use model. This comparison does not only give us information on approximate energy consumption during manufacturing, but also tells us how good our ''representative production technology'' selections were.

We can start our comparison from the first row in Table 7, e.g. the fuel total. It shows that the fuel consumption estimate from the energy end-use model is 37 PJ, whereas it is 20 PJ from the energy process-step models. The possible explanation for the difference is the lack of data on fuel consumption in the production of cryogenic nitrogen, non-cryogenic nitrogen, cryogenic oxygen, non-cryogenic oxygen and fluorocarbons. If we look at the grand total at the very last row of Table 7, we see that we do have information on the total energy consumption for these industrial gases, but we do not know ''what form of energy is that total made out of'', e.g. is it steam?, or is it electricity?, etc. If we allocate the corresponding total energy at the very last row of Table 7 among the fuel, steam & waste heat, and electricity accordingly, we may obtain an estimate close to 37 PJ.

If we look at the total steam and waste heat consumption row in Table 7, we see that the energy end-use model estimates 19 PJ energy consumption, whereas energy process-step models estimate 16.5 PJ. The explanation for this difference

Table 7 – Comparison of energy end-use model values in Fig. 2 and the energy process-step models values for each industrial gas, 1998, PJ

	End-use model	Process-step model	C_2H_2	CO_2	N_2-C	N_2-NC	O_2-C	O_2-NC	Ar	H_2	F
Fuel total	37	20	4	0	NA	NA	NA	NA	0	16	NA
Process heating	22	20	4	0	–	–	–	–	0	16	–
Process cooling and refrigerating	0	0	0	0	–	–	–	–	0	0	–
Machine drive	15	0	0	0	–	–	–	–	0	0	–
Electrochemical processing	0	0	0	0	–	–	–	–	0	0	–
Other process uses	0	0	0	0	–	–	–	–	0	0	–
Steam & waste heat total	19	16.5	2	3.5	NA	NA	NA	NA	0	11	NA
Process heating	11	3	0	0	–	–	–	–	0	3	–
Process cooling and refrigerating	0	8	0	0	–	–	–	–	0	8	–
Machine drive	8	0	0	0	–	–	–	–	0	0	–
Electrochemical processing	0	0	0	0	–	–	–	–	0	0	–
Other process uses	0	5.5	2	3.5	–	–	–	–	0	<1	–
Electricity total	116	124	<1	2	NA	NA	NA	48	74	<1	NA
Process heating	1	0	0	0	–	–	–	0	0	0	–
Process cooling and refrigerating	3	2	0	0	–	–	–	0	2	0	–
Machine drive	111	71	<1	2	–	–	–	0	69	<1	–
Electrochemical processing	1	<1	<1	0	–	–	–	0	0	0	–
Other process uses	0	51	<1	0	–	–	–	48	3	0	–
Grand total	172	169.5	5.8	5.5	6.5	<0.1	1.2	48	74	28	0.4

F, fluorocarbon; NA, not available; C, cryogenic; NC, non-cryogenic.

would be same as the explanation we made for the total fuel consumption above.

The electricity consumption estimate made in energy end-use model is 116 PJ, whereas it is 124 PJ in energy process-step models as both seen in Table 7. The possible reason for seeing a higher estimate in energy process-step models is more likely because of the inaccuracy of the argon energy process-step model. As it is seen in Table 7, cryogenic argon production process requires electricity consumption only. If we assume that cryogenic nitrogen and cryogenic oxygen processes also require electricity only, then we can extract the grand total energy consumption for these processes from the last row of Table 7 to add them into the "electricity total" row of Table 7. This assumption results in 6.5 PJ + 1.2 PJ = 7.7 PJ total electricity being required to produce nitrogen and oxygen cryogenically. If we compare this with the electricity consumption in cryogenic argon production, we see that the Drexel model based argon process-step model's estimate is very much higher than the total electricity requirement estimate of cryogenic nitrogen and oxygen. However, if we remove the argon process-step model estimate from the "electricity total" row in Table 7 – since it is inaccurate – then we have 124 PJ − 74 PJ = 50 PJ, which is very much smaller than the energy end-use model estimate of 116 PJ. Even if we include the 7.7 PJ cryogenic nitrogen and oxygen electricity consumption into the total, we still have 50 PJ + 7.7 PJ = 57.7 PJ. Therefore, it may suggest that argon production may require more electricity consumption relative to other industrial gases. It would be, for example, because it may require very high purity, which requires large amount of energy consumption. Or it could be due to another process related reason which would be a good research topic for someone else. In conclusion, the difference between the energy end-use model estimate for electricity and the energy process-step models estimates for electricity is very large unless we account the argon process-step model. This may suggest that the argon process-step model has been useful in terms of bringing the question of "larger electricity consumption possibility" during argon production.

Finally, if we look at the grand total at the last row of Table 7, we see that the energy end-use estimate is 172 PJ, whereas the energy process-step models estimate is 169.5 PJ. This shows that the energy consumption estimates for process end-uses by energy end-use model and by energy process-step models have very close agreement. This may suggest that the selection of "representative" processes were able to provide us an overall sight about this sector. This may also suggest that the argon process-step model may have some reasonable level of accuracy.

7. Summary

Explanation on how to obtain energy inputs values for hydrogen production using energy end-use model was given in Section 5 in detail. If we rephrase the given methodology in words: the energy end-use model for the Industrial Gas Manufacturing sector gives us the "total" energy consumption for CO_2, nitrogen, oxygen, acetylene, argon, hydrogen, and fluorocarbons. If we want to know how much energy it takes to produce each of these products, we cannot simply divide energy values in the energy end-use model into "seven" to obtain energy consumption values for CO_2, nitrogen, oxygen, acetylene, argon, hydrogen, and fluorocarbons separately. Because, energy consumption to produce, say 1 kg CO_2, is different than the energy consumption amount for 1 kg acetylene production, etc. In addition, forms of energy are different as well, e.g. some processes consume energy in the form of fuel, whereas some consume in the form of electricity. Therefore, each product of Industrial Gas Manufacturing sector has its own unique production process. However, whatever the energy consumption amount to manufacture each product of this sector, the "total" should be equal to what we get in the energy end-use model.

Although energy end-use model gives us the "total" energy consumption for process purposes for all products of the sector, energy inputs for "each product" must be separately identified, e.g. energy inputs for CO_2 production, energy inputs for acetylene production, energy inputs for nitrogen production, etc. The energy flow model that gives us process level of detailed energy consumption information for "each product" is the energy process-step model. Therefore, energy consumption amount at each process step of hydrogen production is given by the energy process-step model for hydrogen production, not the energy end-use model. However, energy end-use model is needed to cross check the energy process-step models, e.g. once we create energy process-step model for each product of the sector, summation of the energy values in the energy process-step models for seven products of the sector should be equal to the total energy consumption amount given in the energy end-use model for process purposes use.

The energy end-use model is not only used for validating the energy process-step model, but also to re-scale or calibrate the energy process-step models to reflect closer agreement with the actual operating data. For example, the dominant hydrogen production technique in industry is the steam reforming of methane. Although the process steps of steam reforming methane is very similar in all hydrogen producing plants, there would still be slight changes in energy consumption at process step level. Since it is not practical to include hydrogen production processes of all plants in the U.S., instead, we can choose "representative process steps" and then we can calibrate them against the national data to obtain an overall representation of hydrogen production in the U.S. In this paper, "representative" hydrogen production process steps were taken from the Drexel models and scaled as it was stated in Section 5.

In order to be able to cross check the accuracy of the national scale hydrogen energy process-step model with the energy end-use model, we need energy process-step models for all products of the Industrial Gas Manufacturing sector, so that we can have the total amount to compare with the energy end-use model. This task has been done as part of Ref. [26]. However, due to the space restrictions, we cannot give material and energy flow models of the products of this sector in this paper. Instead, we can refer to Table 7, which was inserted from Ref. [26], giving us the summary of the energy process step flow models for CO_2, nitrogen, oxygen, acetylene, argon, hydrogen, and fluorocarbons.

As it is seen in Table 7, the summation of energy inputs for CO_2, nitrogen, oxygen, acetylene, argon, hydrogen, and fluorocarbons is very close to what energy end-use model for the whole sector gives us. This shows that the "representative" process steps were selected properly. However, they can still be iterated using the energy end-use model values, so that they exactly match with the actual operating data. That task is out of the scope of this paper.

The methodology used in this paper can be applied to calibrate the process-step models on a national scale for other products of other industries. One can refer Ref. [14] to see the application of this methodology for the U.S. Paper Industry and Ref. [15] for an example of application of this methodology in the petroleum industry.

8. Conclusions

Energy and material flow models of hydrogen production in the U.S. Chemical Industry were presented and the energy process-step model was validated by comparison with the energy end-use model. The Drexel hydrogen production flow model was assumed as the representative hydrogen production model. Therefore, it was used for scaling the material input-output values and energy inputs against various national databases in order to obtain a nationally characteristic material and energy flow model for the hydrogen production given in Figs. 3 and 5, respectively. From energy efficiency and energy management point of view, Fig. 5 identifies possible spots for improved energy utilization on a process step basis. For example, process step 5 has the largest energy consumption in the form of fuel, steam and waste heat. During onsite energy audits, this step turns out to be the target for improvement, e.g. better insulation. In addition, identification of the magnitude of the energy consumption on a national scale for this – or any process – at a process step level of detail provides a prospect for economical savings by improving energy utilization at that particular stage. This kind of identification would also motivate research efforts for searching alternative process steps to replace – or to improve – the currently practiced inefficient ones. However, an energy process-step model on a national scale as in Fig. 3 cannot be created without having an energy end-use model first. This is why we start with creating the energy end-use model in Figs. 1 and 2 to show the overall energy allocation for process end-uses in the sector. Since the energy allocation given in Figs. 1 and 2 is given for the whole sector, it has to be split among each product manufactured by that sector so that we can see how much of that energy input consumed for, let's say, hydrogen production, or acetylene production, etc. This analysis was given in Section 5. The energy process-step model presented in Fig. 2 represents estimated nationwide energy consumption for hydrogen production. The major energy consuming step in hydrogen production was found to be the reformer, which consumes approximately 16 PJ fuel.

As for the energy consumption estimates given in the energy process-step models in Table 7; they were constructed by scaling the various public database and models in the literature on the selected representative production technology for each industrial gas. The selection of the representative production technology for each industrial gas was the major assumption in those models. It should be noted that, even for a particular production technology, there might be many process designs. So, the selection of a representative technology leaves out many of the possibly used process designs from the analysis. Therefore, the numbers in these models probably may involve some level of inaccuracy. However, as it is seen in Table 7, the energy consumption values found in energy end-use model are close to the energy consumption estimates made by the energy process-step models. We can summarize the comparison of energy process-step model values as follows:

→ Energy end-use model estimates are very close to the energy process-step models estimates.
→ Energy consumption distribution among nitrogen, oxygen and argon production is unknown.
→ Due to the complication of this sector, it was still possible to gain an overall sight about the estimate energy consumption for processes.
→ Energy flow model in this paper can be improved to obtain closer estimates on this sector by refining the assumptions, accounting more than one representative process and searching for more data in the future.

To sum up, the energy and material flow models for hydrogen production given in this paper are more likely a very close representative of the actual numbers. The methodology used in this paper can be applied to calibrate the process-step models on a national scale for other products of other industries.

Acknowledgments

This research was supported by the U.S. Department of Energy through Battelle Pacific Northwest National Laboratory under Task Order 11457 of Master Agreement 6630 and through a research agreement with the American Institute of Chemical Engineers. I would like to thank Professor Barry I. Hyman of University of Washington Mechanical Engineering Department for his advice, Professor Bradley R. Holt of University of Washington Chemical Engineering Department for his constructive feedbacks and Dr. Joseph M. Roop of the Pacific Northwest National Laboratory for his vital comments during the course of this research.

REFERENCES

[1] Padró CEG, Keller JO. Hydrogen energy. Kirk-Othmer encyclopedia of chemical technology; 2005.
[2] Muradov NZ, Veziroglu TN. From hydrocarbon to hydrogen–carbon to hydrogen economy. International Journal of Hydrogen Energy 2005;30:225–37.
[3] Baade WF, Parekh UN, Raman VS. Hydrogen. Kirk-Othmer encyclopedia of chemical technology; 2001.
[4] Häussinger P, Lohmüller R, Watson AM. Hydrogen. Ullmann's encyclopedia of industrial chemistry; 2000.

[5] Shreve RN, Brink JA. Shreve's chemical process industries. McGraw Hill; 1984.
[6] Koroneos C, Dompros A, Roumbas G, Moussipoulos N. Life cycle assessment of hydrogen fuel production processes. International Journal of Hydrogen Energy 2004;29:1443–50.
[7] U.S. Census Current Industrial Reports, Table 2a and Table 2b. Available from: http://www.census.gov/industry/1/mq325c045.pdf.
[8] Brown HL, Hamel BB, Hedman BA. Energy analysis of 108 industrial processes. Atlanta, GA: Fairmont Press; 1996.
[9] Worrell E, Phylipsen D, Einstein D, Martin N. Energy use and energy intensity of the U.S. Chemical Industry; 2000. Ernest Orlando Lawrence Berkeley National Laboratory Report. Reference No. LBNL-44314.
[10] Wang M, Lee H, Molburg J. Allocation of energy use in petroleum refineries to petroleum products: implications for life-cycle energy use and emission inventory of petroleum transportation fuels. International Journal of Life Cycle Assessment 2004;9(1):34–44.
[11] Arthur D Little, Inc. (ADL). Overview of energy flow for industries in standard industrial classifications; 2000. Report to the U.S. Department of Energy Office of Industrial Technology. Reference No. DOE/OIT – 71563.
[12] Giraldo L, Hyman B. An energy process-step model for manufacturing paper and paperboard. Energy 1996;21(7/8):667–81.
[13] Andersen JP, Hyman B. Energy and material flow models for the US steel industry. Energy 2001;26:137–59.
[14] Ozalp N, Hyman B. Energy end-use model of paper manufacturing in the U.S. Applied Thermal Engineering 2006;26:540–8.
[15] Ozalp N, Hyman B. Allocation of energy inputs among the end-uses in the U.S. petroleum and coal products industry. Energy 2007;32:1460–70.
[16] U.S. Chemical Industry subsectors according to the North American Industrial Classification Systems (NAICS). Available from: http://www.census.gov/epcd/ec97/industry/E325.HTM [The U.S. Census Bureau website].
[17] Department of Commerce (DOC). Industry economic accounts. Benchmark input–output data. Available from: http://www.bea.gov/bea/dn2/i-o_benchmark_1997.htm; 1997.
[18] Manufacturing Energy Consumption Survey (MECS) by the Energy Information Administration of the U.S. Department of Energy. Available from: http://www.eia.doe.gov/emeu/mecs/.
[19] Ozalp N. Modeling industrial energy flow on a national scale. Proceedings of the International Conference on Harnessing Technology (ICHET); October 2008.
[20] Energy Information Administration (EIA) 860B database: annual electric generator-nonutility. Available from: http://www.eia.doe.gov/cneaf/electricity/page/eia860b.html.
[21] McKay G, Holland CR. Energy savings from steam losses on an oil refinery. Engineering Costs and Production Economics 2001;5:193–203.
[22] Bhatt SM. Energy audit case studies. I – steam systems. Applied Thermal Engineering 2000;20:285–96.
[23] Petek J, Glavic P. An integral approach to waste minimization in process industries. Resources Conservation and Recycling 1996;17(3):169–88.
[24] Ozalp N, Hyman B. Calibrated models of on-site power and steam production in U.S. manufacturing industries. Applied Thermal Engineering 2006;26:530–9.
[25] Simpson A, Lutz AE. Exergy analysis of hydrogen production via steam methane reforming. International Journal of Hydrogen Energy 2007;32:4811–20.
[26] U.S. Census Bureau Current Industrial Reports (CIR). Industrial gases; 1998. Reference No. MA325C(98)-1.
[27] Ozalp N. Energy, material and emissions flow models of the U.S. Chemical Industry. Ph.D. dissertation, University of Washington, Mechanical Engineering Department. Available at the electronic library of the University of Washington, Seattle; December 2005.